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(54) Title: POLYMER COMPOSITIONS SUITABLE FOR MICROWAVE COOKING APPLICATIONS

(57) Abstract: A composition comprising at least one high temperature polymer and a heating effective amount of at least one microwave susceptible filler. Cookware comprising such composition is particularly useful in cooking foodstuffs, requiring browning, particularly pizza and the like.

POLYMER COMPOSITIONS SUITABLE FOR
MICROWAVE COOKING APPLICATIONS

This application claims the benefit of U.S. Provisional Application No. 60/162,461, filed October 29, 1999.

5 This invention relates to cookware, and more particularly to cookware useful in microwave ovens. Still more particularly, the invention relates to cookware for use in microwave processing of foodstuffs, particularly pizzas and the like, and to filled compositions therefor containing high temperature resin and a radiation absorbent filler, preferably carbon fiber.

10 Filled compositions according to the invention absorb microwave energy and are thereby heated. Such compositions may be particularly useful in the fabrication of oven cookware adapted for cooking food in a microwave oven, for example cooking trays, sheets, pans, dishes, casseroles, and the like.

Background of the Invention

15 Conventional methods of heating and cooking food, whether by grilling, boiling, baking or frying, supply heat to the food externally. The surface of the food becomes heated, establishing a temperature gradient from the surface to the interior. Heat is transferred from the surface to the interior by thermal diffusion, so that the coldest point approaches the warmest temperature of the system with time. When
20 the internal temperature reaches the desired final temperature, the cooking or heating process is complete. The maximum temperature of the food is limited by the temperature of the heating medium. For example, food immersed in water at ambient pressures may reach the boiling point of water, 100 °C, and no more.

 The surface of food cooked by conventional heating methods will be
25 maintained at the highest temperature and thus heated for the greatest length of time. Generally food surfaces will take on an appearance and texture characteristic of the cooking method. For example, meats that are grilled will have seared surfaces, baked breads will have crusts, and fried foods may be crisp. While the particulars will vary from culture to culture, the acceptability of foods turns on having
30 a proper surface appearance, based on preferences that develop or are acquired over many generations.

 More recently, microwave heating has become used for cooking and reheating foods and is widely accepted for its rapid heating of foods and ease of use. In

microwave heating, food is exposed to high frequency electromagnetic radiation. Water molecules contained within the food, due to their dipolar nature, try to follow the very high frequency oscillations of the electric field associated with the electromagnetic radiation, and thus are heated. When there is little or no water present in the foodstuff, or the water becomes substantially lost by evaporation, no further heating can occur.

Although food cannot be heated above about 100 °C in home and food service microwave ovens, the temperatures are sufficiently high for reheating cooked food, and the ovens will cook most foods adequately. However, microwave heating tends to cause foods to soften, producing undesirable changes in texture. Browning and other surface effects attained with conventional cookery, which are essential to acceptability are not directly reproduced by microwave heating. The food surfaces do not reach the high temperatures encountered during conventional cookery; indeed, the surface of food heated in a microwave oven often is at a lower temperature than the interior due to external cooling. Foods cooked in microwave ovens thus do not resemble the products of conventional cookery and, even though fully cooked and safely edible, may be thought unappetizing and unpalatable.

One of the most popular frozen entrees is pizza, constructed of a lower crust layer of dough and an upper topping layer including a mixture of various substances, generally cheese, tomato sauce and meat. The topping materials are selected to provide a variety of products for the consuming public. Commonly the crust is baked, and the topping is added in an uncooked, usually frozen condition, intended to extend their shelf life. For the best consumer acceptance from a taste and texture sense, such layered food products or articles should be thawed and then baked by some heating appliance that will restore the desired reconstituted texture and condition. Due to the characteristics of the crust, high quality reconstitution is accomplished only by heating in a convection oven. The standard convection oven produces a crunchy, high quality crust that is crisp with a topping cooked to duplicate fresh, hand made pizza.

Attempts to reconstitute pizza by microwave heating have been less satisfactory, producing pizza having a compromised ultimate quality when compared with pizza reconstituted only in a convection oven. Using a microwave oven to bake or cook frozen pizza definitely shortens the cooking time; however, the texture is

deteriorated and the crust has almost no crispness or crunchiness. Generally, providing sufficient heat to make the crust crisp tends to overcook the topping material. Delay in eating the pizza may cause the crust to become hard and brittle and the product generally loses its resiliency, turning leathery and causing the hot
5 sauces forming part of the topping to migrate into the cells of the prebaked crust.

Loss of crispness and texture in reheating foods, including pizza, has been addressed by packaging design. Such packaging may include ribs or protrusions to support the food within and allow air circulation to remove vapors from the surface. Materials employed for such packaging frequently are thermoplastic sheet materials
10 containing radiation absorbent filler, for example, carbon black, graphitic particles, comminuted carbon fiber particles or the like. The filler absorbs microwave energy, undergoing dielectric heating and thereby raising the temperature of the container or packaging. Such packaging continues to transmit heat to the food after the microwave irradiation cycle has been completed, reducing the occurrence of cold
15 spots in the food and enhancing drying and crisping.

Packaging designs particularly suited for use in reheating pizza may include a microwave susceptor sheet on or spaced from the lower wall of the microwave oven to serve as a plate or platform. Susceptors generally comprise a layered sheet stock with layers having a metallized surface or formed of other conductive material to
20 absorb microwave energy. Placed in the energy field of a microwave oven, susceptors undergo inductive heating, reaching temperatures above 100 °C, and thus may be designed to remove moisture and enhance drying and crisping during heating.

The materials disclosed in the art for the construction of such improved
25 packaging have generally included cellulosic sheet stock and filled thermoplastics including polyethylene, polypropylene and polyesters such as polyethylene terephthalate and the like. Although the improved packaging may have some capability for producing higher temperatures needed for browning and similar processing of foods, generally, the packaging has been intended for use in reheating
30 pre-cooked foods requiring crisping and for cooking foods that can be successfully processed at moderate temperatures, i.e. temperatures that do not much exceed about 100°C.

Filled ceramic composite materials capable of attaining high temperatures when irradiated with microwave energy are also known. For example, self-heating structures comprising silicon carbide filled with a microwave susceptible filler such as carbon fiber, alumina fiber or the like have been disclosed for use in microwave cooking. When irradiated in a microwave oven, these self-heating structures may attain temperatures as great as 500°C. Surfaces of food in contact with such a vessel will thus be rapidly heated, much as in a conventional oven, while the internal temperature becomes rapidly increased through microwave heating, cooking the food. The resulting food product may thus be appropriately cooked throughout and simultaneously provided the desired browned or seared surface. Similar structures have been used in processing pizza. In this, use the self-heating vitrocera-
mic disc or plate is irradiated with microwaves and preheated to a temperature near 300 °C. Raw pizza base or crust is placed on the plate and allowed to precook, thereby pasteurizing the crust and providing a crisped or browned lower surface. The base is then removed from the plate, provided with the topping and stored for subsequent final cooking in a conventional convection oven.

Vitrocera-
mic plates are generally somewhat brittle, thus subject to damage and breakage, and are heavy and are thus more difficult to use and inconvenient to store. Moreover, filled ceramic materials and particularly fiber filled silicon carbide structures require complex operations to produce and may not be readily formed into attractive utensils.

The convenience of a microwave oven has thus allowed the consumer to rapidly and easily reheat prepared foods, for example, by simply removing a frozen food item from the consumer's freezer and heating the item in the microwave oven. Heating and cooking with microwave ovens has been more limited to processing soft foods and foods with gravies, sauces and the like that do not require browning or crisping. There remains a great need in the art for improved materials that permit using microwave heating to heat or cook foods needing browning and crisping such as, for example, pizza, hashbrown potatoes, fish sticks and the like, and for cooking utensils and containers comprising such improved materials.

Summary of the Invention

This invention is directed to improved polymer compositions suitable for use in food cooking applications, said compositions comprising at least one high temperature polymeric material and a heating effective amount of at least one microwave susceptible filler material suitable for use as microwave temperature enhancing material. The invented compositions are useful in providing cookware suitable for microwave use; hence, the invention is further directed to microwave cookware and to a method for making such cookware. The invention may also be viewed as directed to a method for preparing food wherein the food is placed in or on cookware comprising at least one high temperature polymeric material and a heating effective amount of at least one microwave susceptible filler.

As used herein, the term "heating effective amount" means an amount of microwave susceptible filler that, when subjected to microwave radiation, will cause the temperature of the cookware comprising the filler to increase to a temperature such that the cookware will heat, cook or preferably brown food placed in or on the cookware but not result in the melting or excessive softening of the polymeric material during such heating, cooking or browning.

Detailed Description of the Invention

The improved polymer compositions according to this invention are filled polymers comprising a high temperature polymer and microwave susceptible filler.

High temperature polymers or resins useful in forming the compositions and cookware of this invention are polymers that have high temperature properties sufficient to withstand temperatures typically necessary to heat food to a temperature suitable for cooking and particularly for browning the surfaces thereof. Crystalline or partially crystalline thermoplastic polymers having a melting point (T_m) of at least about 140°C, preferably at least about 200°C, and most preferably at least about 250°C, and amorphous thermoplastic polymers having a glass transition temperature (T_g) of at least about 140°C, preferably of at least about 200°C and more preferably of at least about 250°C will generally be suitable for the purposes of this invention. Generally, where rapid browning of meats and the like with brief exposure to heat is desired, temperatures well in excess of 250°C to as great as 350°C or greater may be encountered, necessitating the use of crosslinked and thermoset resins and the like. Such resins thus may also be found useful, provided the thermal decomposition

temperature of the resin is greater than us temperature envisioned, i.e. greater than about 250 to 350°C.

T_g and T_m are conventionally determined in the art, as are polymer thermal decomposition temperatures, using standardized thermogravimetric analysis methods. For the purposes of describing and characterizing compositions according to this invention, differential scanning calorimetry (DSC) procedures conducted at a heating rate of 20°C per minute are conveniently employed.

Polymers having high temperature properties suitable for use in the practice of this invention may include poly(arylether sulfones), polysulfones, aromatic polyesters, polycarbonates, poly(arylether ketones), polyetherimides, aliphatic, partially aromatic and aromatic polyamides, polyimides, particularly aromatic polyimides, and the like. Particularly preferred are the aromatic polyesters and the poly(arylether sulfones).

Poly(arylether sulfones) are well known in the art. Suitable commercial examples of such polymers include Udel and Radel thermoplastics available from BP Amoco Polymers, Inc. Poly(arylether sulfones) that may be found useful in the practice of this invention are further described in the art, for example, in U.S. Patent 4,293,670 and in Canadian Patent 847,963. Aromatic polyesters, particularly liquid crystalline aromatic polyesters, that may be useful in the practice of this invention are also well known in the art, and include for example, Xydar liquid crystal polymers commercially available from BP Amoco Polymers, Inc. Particularly useful and suitable are Xydar SRT-400 and Xydar SRT-900 liquid crystal polymers. These Xydar thermoplastic polymers are wholly aromatic polyesters made by polymerizing a mixture of terephthalic, isophthalic and p-hydroxybenzoic acid with biphenol. Aromatic polyesters suitable for use in this invention and methods for their manufacture are disclosed in U.S. Patents 3,637,595; 4,503,168; 4,563,508; and 4,626,557.

Polyetherimides are also well known high temperature polymeric materials, and polyetherimides suitable for use and available from the trade include Ultem thermoplastics, manufactured by the General Electric Company. Additional polyetherimides and methods for their manufacture are disclosed in U.S. Patent 4,293,670 and in U.S. Patent 4,503,168.

Poly(arylether ketones) useful in the practice of this invention are available commercially from BP Amoco Polymers, Inc. and from Victrex. Examples of useful

poly(arylether ketones) and methods for their manufacture are disclosed, for example, in U.S. Patent 4,713,426.

Aromatic and partially aromatic polyamides may also be found useful in the practice of this invention. Such polyamides are commercially available from BP
5 Amoco Polymers, Inc. under the name Amodel, and methods for making aromatic and partially aromatic polyamides, as well as examples of suitable aromatic and partially aromatic polyamides, are disclosed and described in U.S. Patent Reissue 34,447. Aromatic polycarbonates may also be found useful in some applications according to this invention, and are commercially available from the General Electric
10 Company under the name Lexan and from the Bayer Corporation. Polycarbonates and method for their manufacture are disclosed and described in U.S. Patents 4,018,750; 4,123,436, and 3,153,008. The U.S. Patents and Canadian Patent recited above are hereby incorporated by reference in their entirety.

It will be understood that when in use, the compositions according to this
15 invention will directly contact the food being heated. Foods, and particularly foods that are wet or produce juices and other fluids on heating, tend to extract and dissolve lower molecular weight components including plasticizer, residual monomer, stabilizing additives and the like from resin formulations. In addition, some resins may be subject to hydrolytic attack by moisture and by food components that are
20 acidic or strongly alkaline, and may even chemically react with the food components at elevated temperatures. Thus, it will be necessary that the resin formulations be selected to be resistant to such interaction with foods, and contain only grades of resins and fillers, and additive components, if any are included, that are deemed acceptable for such use. Generally, plastic materials intended for use in food contact
25 applications are provided by resin manufacturers in particular grades formulated to be suitable for food use. Approved, food-grade versions of lower temperature thermoplastics including polyethylene and polypropylene, as well as polyethylene terephthalate, are widely available. Grades of Xydar liquid crystal thermoplastics deemed suitable for food contact are also available, and suitable grades of other high
30 temperature thermoplastics, including poly(arylether sulfones), polycarbonates and polyether imides, may also be available.

Generally described, microwave susceptible fillers are electrically conductive particulates that absorb microwave energy and thereby become heated. Fillers

suitable for use in the practice of this invention include metals in finely divided form such as, for example, powdered elemental iron, tin, copper, aluminum, silver or the like, either as elemental metals or in the form of oxides. Metal salts such as, for example, hydroxides, halides such as chlorides or bromides, sulfates and the like
5 may also be found useful; preferably such compounds will be insoluble and not subject to being leached by foods or when immersed in water such as during cleaning operations.

Particulate carbon, and particularly carbon fibers are particularly suitable for use as microwave susceptible fillers. Carbon in the form of carbon black or similarly
10 finely divided particles may be used. More preferred will be carbon that is at least partially, for example at least about 50 weight percent, more preferably at least about 75 weight percent, graphitic, and still more preferably substantially entirely graphitic, and most preferably will be particulate in form.

Carbon fiber manufactured from pitch or from a synthetic source such as
15 polyacrylonitrile (PAN) fibers is particularly useful. Graphitized pitch-based carbon fiber containing at least about 50 weight percent graphitic carbon, more preferably greater than about 75 weight percent graphitic carbon and up to substantially 100% graphitic carbon is readily available from commercial sources. Highly graphitic carbon fiber particularly suitable for use in the practice of this invention may be
20 further characterized as highly conductive, and such fiber is generally supplied having a modulus of about 80 to about 120, more preferably about 100 to about 115 million pounds per square inch, i.e., million lbs/in² (MSI).

Carbon fiber may be employed as chopped carbon fiber, or in other particulate form such as may be obtained by milling or comminuting the fiber.

25 The amount of microwave susceptible filler employed for the compositions according to the invention will depend in part upon the nature of the filler selected. More highly conductive fillers such as highly graphitized carbon fiber and metals will be employed at lower levels than less susceptible fillers including carbon black, metal oxides and the like. Generally, the amount employed will be selected to raise the
30 temperature of cookware surfaces in contact with the pizza or other foodstuff, or in close proximity thereto, to a level sufficient to produce browning or scorching, without causing undesirable burning or damage to the cookware. Surface temperatures suitable for these purposes lie in the range of from about 180°C to the upper use

temperature of the resin component, and preferably from about 200°C to about 260°C. While it is believed to be essential that the browning or cooking temperature be reached quickly, compositions with an excessive amount of susceptible filler may continue to rapidly increase in temperature and reach temperatures above a level
5 considered safe for such ovens. In addition, compositions containing high levels of conductive filler tend to reflect microwave radiation and may thereby cause damage to the oven. Hence the level of filler will also be selected with a consideration of the envisioned enduse. Preferably articles comprising the filled composition will withstand normal heating cycles of from about 1 to about 20 minutes without
10 exceeding a safe upper temperature or causing damage to the oven.

For compositions comprised of a resin selected from the higher temperature resins suitable for food contact use and resistant to hydrolytic or other attack by food components, the amount of microwave susceptible filler employed will preferably lie in the range of from about 0.1 to about 10.0 wt%, more preferably from about 0.2 to
15 about 5 wt%, and still more preferably from about 0.5 to about 5 wt%, based on combined weight of filler and polymer. As noted, more conductive fillers including graphitic carbon fibers will be employed at levels at the lower end of these preferred ranges, preferably in amounts of from about 0.5 to about 4 wt%. Fillers may be employed singly or in combination; for example, comminuted carbon fiber may be
20 combined with pigment grade carbon black to provide a suitably pigmented composition having the desired thermal properties together with an attractive color and appearance.

In addition to high temperature resin and microwave susceptible filler, compositions according to the invention may include other additives and components
25 that are not considered microwave susceptible fillers such as talc or other mineral fillers and reinforcing fillers, non-conductive fibers or the like at levels sufficient to improve mechanical properties including high temperature strength and rigidity according to common practice in the resin compounding molding arts. Thermal stabilizers, plasticizers, ultraviolet light stabilizers, lubricants, mold release agents,
30 colorants, and other additives and components commonly used in the polymer molding arts may also be included as desired. As noted, it will be understood that only grades of additive components, if any are included, that are deemed acceptable for such use will be employed.

The high temperature resin and microwave susceptible filler, together with such other additive components as may be used, may be blended and extruded according to well known and widely practiced methods and procedures, using standard equipment commonly employed in the polymer blending arts. The polymer compositions of this invention will be further fabricated to form cookware and similar articles using methods and practices commonly used in the plastics fabricating art, including injection molding, blow molding, thermoforming, melt extrusion and the like. Cookware according to the invention may take any convenient form, for example, a pan, a tray, a sheet, a dish, bowl, casserole dish, a pizza stone or any other type of cookware. Trays, sheets and the like are readily produced from the compositions of this invention and may be found suitable for a wide variety of cooking and baking uses; hence such articles will be the most preferred form of cookware.

Examples

Components used in preparing the formulations of the following examples include:

LCP: liquid crystal polymer, an aromatic polyester having a melting point of 350°C, obtained as Xydar SRT 900 resin from BP Amoco Polymers, Inc.

Talc: obtained as Vertal 1000 from Luzenac America, Inc.

Carbon fiber: comminuted graphitized carbon fiber, obtained as ThermalGraph DKXD from BP Amoco Polymers, Inc.

Examples 1-4 and Comparison Example: Formulations according to the invention, together with control formulations, were prepared and molded to provide 3 in. by 2 in. by 1/8 in. thick plates for thermal testing. The compositions are summarized in Table I, below. The formulations further included as colorants pigment grades of 0.25 pph titanium dioxide, 0.32 pph Channel black, 0.55 pph Kelly Green and 2.0 pph Lightfast Yellow, based on 100 parts combined weight of LCP, Talc and Carbon Fiber.

TABLE I

Ex. No.:	C-1	1	2	3	4
LCP wt%	55	55	55	55	55
Carbon Fiber wt%	-	2	4	6	8
Talc wt%	45	43	41	39	37

The plates were placed in a microwave oven rated at 1000 watts and exposed to microwave radiation for 10 minutes. The plates of Examples 1-4 reached a high temperature, as determined by touch; the plate of the Comparative Example did not significantly increase in temperature.

Additional plates were molded from a composition substantially as shown in Examples 1 and 2. The molded plates were used to cook commercial pizza comprising a dough crust and a topping, the topping comprising cheese and a tomato-based sauce. After approximately 5 min. of heating, the pizza was found to have an acceptably browned surface, together with an adequately cooked topping.

Examples 5 - 11 Additional formulations according to the invention were prepared and molded to provide 3 in. by 2 in. by 1/8 in. thick plates for thermal testing. The molded plates were placed in a microwave oven rated at 1000 watts and the surface temperature of each was measured with thermocouples as each was exposed to microwave radiation. Total time required to reach 200 °C and then exceed 260° C was recorded.

The compositions and test results are summarized in Table II, below.

TABLE II

Ex. No.:	C-2	5	6	7	8	9	10	11	12
LCP wt%	55	55	55	55	55	55	55	55	55
Talc wt%	45	44.5	44	43.5	43	42.8	42.5	42	41.5
Carbon Fiber wt%	-	0.5	1.0	1.5	2.0	2.2	2.5	3.0	3.5
Carbon Black pph	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
Time min.	> 10	> 10	> 10	> 10	9*	> 10	6	4.5	3.8

Notes: * An additional sample tested at > 10 min.

It will be seen that maintaining the test plate for more than 10 minutes without exceeding the limit temperature of 260 °C requires the level of susceptible filler be less than about 2.5 wt% of the combined weight of resin, fiber and talc, or 4.4 wt% based on combined weight of resin and carbon fiber. Inasmuch as carbon black is

somewhat conductive and thus also susceptible to microwave heating, compositions with increased levels of carbon black were evaluated.

Examples 12 - 21 Additional formulations according to the invention were prepared and molded to provide 3 in. by 2 in. by 1/8 in. thick plates for thermal testing. The molded plates were placed in a microwave oven rated at 1000 watts and the surface temperature of each was measured with thermocouples as each was exposed to microwave radiation. Total time required to reach 200 °C and then exceed 260° C was recorded.

The compositions and test results are summarized in Table III, below.

10

TABLE III

Ex. No.:	13	14	15	16	17	18	19	20	21
LCP wt%	55	55	55	55	55	55	55	55	55
Talc wt%	44.1	44.1	44.1	44	44	44	43.9	43.9	43.9
Carbon Fiber wt%	0.9	0.9	0.9	1.0	1.0	1.0	1.1	1.1	1.1
Carbon Black pph	1.4	1.5	1.6	1.4	1.5	1.6	1.4	1.5	1.6
Time min.	4	4.75	3.5	5	5	6.25	7.75	6	5

An additional sample, comprising 1.2 wt% carbon fiber and 1.4 pph carbon black was molded and tested, producing a heating time of 3.25 min.

Compare the heating behavior of the specimens of Examples 13-21 with the specimen of Example 6 comprising 1 wt% carbon fiber and 0.32 pph carbon black, having a heating time of over 10 min. The increased level of carbon black will be recognized to have significantly increased the rate of heating. However, it will be apparent that small changes in the levels of carbon fiber and in the levels of carbon black produced rather erratic differences in heating time. Generally, these differences appear to fall within error limits of the measurement techniques employed, and likely arise at least in part from non-uniform dispersion of the carbon black and fiber within the test specimens.

Compositions comprising only carbon fiber as the susceptible filler, i.e. with no carbon black, were also prepared and evaluated.

Examples 22 - 28 Additional formulations according to the invention were prepared and molded as in Examples 5-11 to provide 3 in. by 2 in. by 1/8 in. thick plates for thermal testing. The molded plates were placed in a microwave oven rated at 1000 watts and the surface temperature of each was measured with

thermocouples as each was exposed to microwave radiation. Total times required to reach 200 °C and then to exceed 260° C were determined.

The compositions are summarized in Table IV, below.

TABLE IV

Ex. No.:		22	23	24	25	26	27	28
LCP	wt%	55	54.1	54	53.9	53.8	53.7	53.6
Talc	wt%	45	45	45	45	45	45	45
Carbon Fiber	wt%	0	0.9	1.0	1.1	1.2	1.3	1.4
	wt% on resin and fiber	0	1.6	1.8	2.0	2.2	2.4	2.5

5

For compositions comprising a liquid crystal polymer or polyester resin and graphitic carbon fiber, a level of carbon fiber of about 2 wt%, based on combined weight of resin and fiber, will be suitable for cooking pizza and the like.

The invention will thus be seen to be directed to cookware for use in
 10 microwave processing of foodstuffs, particularly pizzas and the like, and to filled compositions therefor containing high temperature resin and a radiation absorbent filler, preferably carbon fiber. Generally the invented composition will comprise a high temperature polymer, preferably a crystalline or semicrystalline polymer having a crystal melting temperature T_m of at least 180°C, together with a microwave
 15 susceptible filler. Particularly suitable are compositions comprising a liquid crystal polymer having a T_m of from about 200 °C to about 350 °C and a heating effective amount, preferably from about 0.2 to about 5 wt%, of a carbon fiber, preferably a graphitized carbon fiber, in particulate form. The invented composition may further comprise additional fillers including talc and the like as necessary to provide
 20 improved mechanical properties, as well as pigments, colorants, thermal stabilizers, antioxidants and the like according to practices and methods commonly employed in the resin compounding arts.

The invented compositions are useful in the fabrication of cookware, and in molded goods for use in the preparation of foods, and may be particularly useful in
 25 microwave cookery. Such cookware, as well as methods of processing food employing such cookware, are also contemplated as falling within the scope of the invention as disclosed and described herein. Although embodiments of the invention have been set forth in the form of specific examples, these embodiments are

provided by way of illustration of the invention and not in limitation thereof. Further modifications and adaptations of the teachings will be readily apparent to those skilled in the art and are contemplated as within the scope of the invention, which is defined by the following claims.

5

Claims:

1. A composition comprising at least one high temperature polymer selected from the group consisting of amorphous polymers having a glass transition temperature T_g greater than 180 °C and crystalline and partially crystalline polymers having a crystal melt temperature T_m greater than 180 °C, and a heating effective amount of at least one microwave susceptible filler.
2. A composition comprising a crystalline or partially crystalline polymer having a crystal melting temperature T_m of at least about 180°C and a heating effective amount of at least one microwave susceptible filler.
3. The composition of Claim 2 wherein the polymeric material is an aromatic polyester.
4. The composition of Claim 1 wherein the microwave susceptible filler is carbon fiber.
5. A composition comprising an aromatic polyester having a crystal melt temperature T_m greater than 180 °C, and from about 0.2 to about 5 wt% of a microwave susceptible filler, based on combined weight of said filler and said polyester.
6. The composition of Claim 5 wherein the microwave susceptible filler is carbon fiber.
7. The composition of Claim 5 wherein said aromatic polyester is a liquid crystal polymer having a T_m of from about 200 °C to about 350 °C.
8. The composition of Claim 5 wherein said aromatic polyester a liquid crystal polymer having a T_m of from about 200 °C to about 350 °C and said filler is comminuted carbon fiber.
9. A method for preparing food in a microwave oven comprising subjecting food to microwave radiation wherein the food is placed in or on cookware comprising an aromatic polyester having a crystal melt temperature T_m greater than 180 °C and a heating effective amount of carbon fiber.
10. The method of Claim 9 wherein aromatic polyester is a liquid crystal polymer having a T_m of from about 200 °C to about 350 °C.
11. The method of Claim 9 wherein said cookware comprises from about 0.5 to about 5 wt% communitied carbon fiber, based on combined weight of said fiber and said polyester.

12. Cookware suitable for microwave use made from a composition comprising an aromatic polyester having a crystal melt temperature T_m greater than 180 °C and a heating effective amount of carbon fiber.

13. The cookware of Claim 12 wherein said aromatic polyester is a liquid
5 crystal polymer having a T_m of from about 200 °C to about 350 °C and wherein said composition comprises from about 0.5 to about 5 wt% comminuted carbon fiber, based on combined weight of said fiber and said polymer.

14. Molded article adapted for use in microwave ovens comprising a liquid
10 crystal polymer having a T_m of from about 200 °C to about 350 °C and from about 1 to about 5 wt% comminuted carbon fiber, based on combined weight of said fiber and said polymer.

15. The molded article of Claim 14 comprising about 2 wt% said comminuted carbon fiber.

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(54) Title: **POLYESTER OVENWARE FOR MICROWAVE COOKING APPLICATIONS**

(57) Abstract: A composition comprising at least one high temperature polymer and a heating effective amount of at least one microwave susceptible filler. Cookware comprising such composition is particularly useful in cooking foodstuffs, requiring browning, particularly pizza and the like.

INTERNATIONAL SEARCH REPORT

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PCT/US 00/41459

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A47J36/04 C08K7/06 C08K3/04 C08L67/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A47J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 90 03992 A (AMOCO CORP) 19 April 1990 (1990-04-19) claims 1,12,13 ---	1-8, 12-15
X	GB 2 233 661 A (T & N TECHNOLOGY LTD) 16 January 1991 (1991-01-16) claim 1; examples ---	1
X	US 4 851 467 A (FRAYER PAUL D) 25 July 1989 (1989-07-25) claims; examples ---	1-8
X	JP 03 215226 A (MATSUSHITA ELECTRIC IND CO LTD) 20 September 1991 (1991-09-20) claims; examples ---	1,2
	--- -/--	

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 04 009117 A (MATSUSHITA ELECTRIC IND CO LTD) 13 January 1992 (1992-01-13) claims -----	1,2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/41459

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9003992	A	19-04-1990	AT 151099 T	15-04-1997
			AT 156851 T	15-08-1997
			AT 133975 T	15-02-1996
			CA 2000474 A,C	11-04-1990
			CA 2000486 A,C	11-04-1990
			CA 2000487 A,C	11-04-1990
			DE 68925630 D	21-03-1996
			DE 68925630 T	12-09-1996
			DE 68927929 D	07-05-1997
			DE 68927929 T	06-11-1997
			DE 68928258 D	18-09-1997
			DE 68928258 T	26-03-1998
			EP 0395750 A	07-11-1990
			EP 0427795 A	22-05-1991
			EP 0390915 A	10-10-1990
			JP 2966455 B	25-10-1999
			JP 3502818 T	27-06-1991
			JP 2966456 B	25-10-1999
			JP 3501749 T	18-04-1991
			JP 2966457 B	25-10-1999
			JP 3501750 T	18-04-1991
			WO 9004001 A	19-04-1990
			WO 9004003 A	19-04-1990
			US 5097001 A	17-03-1992
			US 5089594 A	18-02-1992
			US 5079289 A	07-01-1992
			US 5147967 A	15-09-1992
			US 5296542 A	22-03-1994
			US 5204417 A	20-04-1993
			US 5216091 A	01-06-1993
			US 5066767 A	19-11-1991
GB 2233661	A	16-01-1991	EP 0406941 A	09-01-1991
US 4851467	A	25-07-1989	AU 8210687 A	26-05-1988
			JP 63254159 A	20-10-1988
JP 03215226	A	20-09-1991	NONE	
JP 04009117	A	13-01-1992	NONE	